Reactively rf magnetron sputtered AlN films as gate dielectric

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AlN films were deposited on silicon (100, 111), fused quartz and GaAs (100) by sputtering in an Ar:N$_2$ gas mixture. We report on the physical and chemical analysis of the films with the aid of scanning electron microscopy, x-ray diffraction, and Auger electron spectroscopy. The films were found to be transparent with a c-axis orientation. Their bulk resistivity was 10^{15} Ω-cm. Quasistatic C-V analysis of Al/AlN/Si gave a flat-band voltage of 0.85 V, density of fixed charge of 6×10^{10} cm^{-2} and a density of fast interface charge of 1.5×10^{11} cm^{-2} eV^{-1} at midgap. These films were formed at 250 °C and offer an attractive fabrication alternative for gate dielectric.

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I. INTRODUCTION

Recently considerable interest has been shown in aluminum nitride (AlN) films because of their optical, electrical, dielectric, and acoustic properties. The chemical and thermal stability as well as high resistivity of the films makes them suitable as insulating and passivating layers in semiconductor devices. Additionally, AlN films have potential application for high frequency monolithic surface acoustic wave (SAW) devices because of their large electromechanical coupling constant and high acoustic velocity. AlN films have been prepared by chemical vapor deposition (CVD),[1,2] ion implantation,[3,4] and ion plating.[5] In these techniques, the substrate temperature during deposition was rather high. For example, Morita et al.[6] have obtained epitaxial growth of AlN on Si using organometallic CVD system at a substrate temperature of 1260 °C. In another CVD system,[7] the films have been deposited by the reaction of aluminum tribromide and ammonia in a temperature range of 600–900 °C. However, for the sake of compatibility with other processing steps in the production of semiconductor devices, there is a need to develop techniques for the deposition of AlN films at temperatures less than 400 °C. Deposition at low temperature reduces the thermal stress in the insulator–semiconductor interface and also allows the fabrication of devices which require a metal electrode beneath the film.

rf or dc sputtering techniques[8-11] are generally used to deposit oriented films at low temperatures. Addition of magnetron capability to the sputtering system confines the secondary electrons emitted from the target. This trapping of the electrons reduces the electron bombardment of the sample surface, and also allows better control of the substrate temperature. Higher sputtering rates are also possible using magnetron sputtering. We report on the deposition of AlN by reactive rf planar magnetron sputtering and its structural analysis by x-ray diffraction (XRD), Auger electron spectroscopy (AES), and scanning electron microscopy (SEM). The electrical properties of Al/AlN/Si have been investigated by both high frequency and quasistatic C-V measurements.

II. FILM GROWTH

In this study, an rf sputtering system (Perkin Elmer 2400 8J) with a magnet assembly was used to prepare AlN films. A target of aluminum with 5N purity and a diameter of 8 in. was used. The sample temperature was determined with a chromel-alumel thermocouple inserted through the side and screwed from the bottom of the substrate holder. The substrate makes thermal contact to the substrate holder. The substrates were thoroughly cleaned just prior to deposition. The cleaning sequence for silicon was the removal of organic impurities (trichloroethylene, acetone, methanol, sulfuric acid/hydrogen peroxide) removal of oxide layer (buffered HF) and the removal of any metallic or ionic impurities (hydrochloric acid/hydrogen peroxide). The substrate heating sequence was started after pumping the chamber to a pressure of 1×10^{-6} Torr. Once the substrate temperature was stabilized and the chamber pressure reduced to 4×10^{-7} Torr, the sputtering gases (Ar and N$_2$) which were premixed using flowmeters were introduced through a precision leak valve. A thermocouple gauge was used to monitor the pressure. The gases at desired pressure and ratios were allowed to flow for 15 min to purge the chamber and also to further stabilize the substrate temperature before sputtering. With the shutter covering the substrate, the target was sputter cleaned for 20 min in argon and in 20 min in the gas mixture. The deposition of the film was started by removing the shutter from the substrate. Various parameters—pressure, temperature and rf power—have been varied for depositing AlN films. Typical deposition parameters are given in Table I. Low rf power (less than 200 W) was used to minimize substrate heating and lattice damage due to electron and ionic bombardment respectively.

III. FILM EVALUATION

A. Physical and chemical properties

The AlN films were evaluated using optical and scanning electron microscopy, x-ray diffraction, and Auger elec-

TABLE I. Typical deposition parameters.

Gas pressure	8 mTorr
Sputtering gases	Ar + N$_2$(20:80)
Target to substrate distance	6 cm
rf power	100–200 W
dc voltage	100 V
Substrate temperature	250 °C
Deposition rate	18 Å/min.
Target	Al-99.999% pure, 8-in. diam.
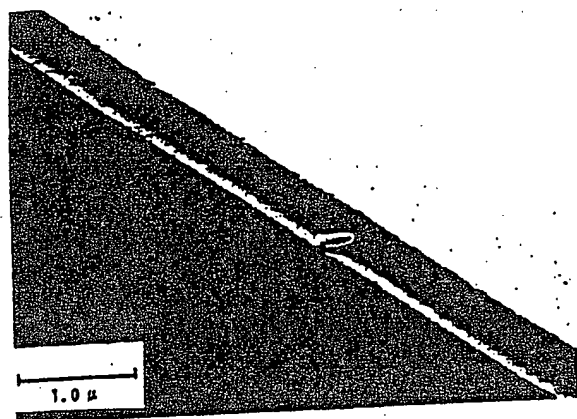
FIG. 1. Scanning electron micrograph of cleaved edge of AlN film on Si, showing the columnar structure.

FIG. 3. Auger spectra in the bulk of the AlN film. The peak at (215 eV) is due to argon which was used to sputter profile the film.

tron spectroscopy. Figure 1 shows a cross section of the AlN/Si film, in which the columnar structure is apparent and which implies a perferred orientation of the film. Films deposited on quartz under various conditions were transparent.

The crystal orientation of the film was determined from x-ray diffraction scans using Cu-Kα radiation. Figure 2 shows the x-ray diffraction pattern of 0.2-μm-thick AlN film deposited on a Si (100) substrate. The presence of only the (002) peak indicates c-axis orientation of the film. The position of the x-ray peak was found to occur at lower angles than that obtained from bulk AlN powder sample (36.038 °C). The instrument alignment and calibration was checked with a standard Si (100) sample before actual measurement. c-axis orientation was also obtained for AlN films deposited on Si (111), GaAs (100), and fused quartz.

An Auger analysis was performed in order to study the bulk and interface composition of the AlN/Si structure. A typical Auger spectra of the film after a two minute sputtering is shown in Fig. 3. From this, it is clear that in the bulk of the AlN film, the only impurity present is oxygen. The amount of oxygen in the bulk was always found to be less than 5%, but at the AlN/Si interface, the oxygen content is
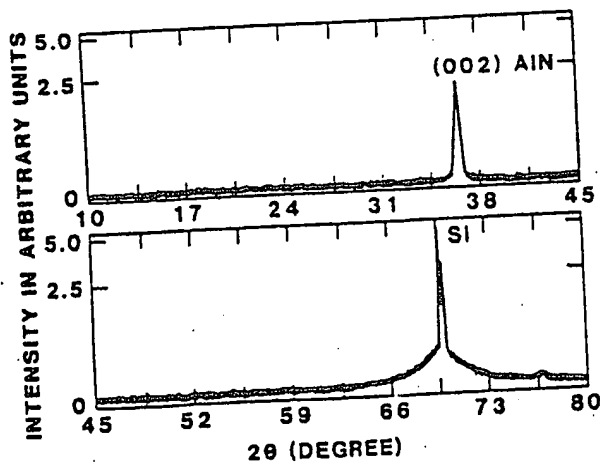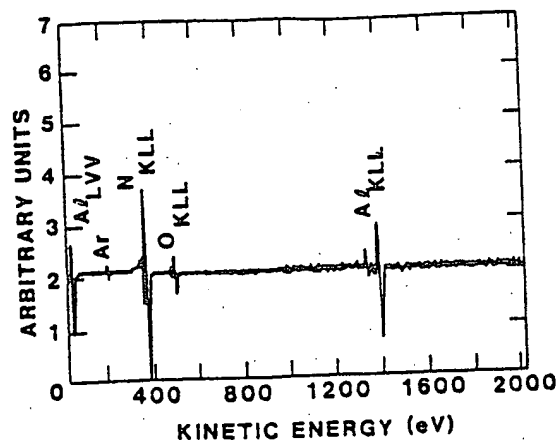
slightly higher because of the thin native oxide on Si surface. Hantzpergue et al.[9] have reported on carbon contamination in their films deposited by reactive sputtering of Al. In the present work, the carbon content is lower than the AES detection limit (1%).

B. Electrical properties

In order to study the dielectric properties of the AlN films, metal-oxide-semiconductor (MIS) structures were fabricated. The gate electrodes with a diameter of 250 μm were made by e-gun or thermal evaporation of aluminum through a metal mask. Subsequently, aluminum was evaporated on the back of the Si wafer in order to obtain an ohmic contact. The MIS structure was heat treated for 30 min in N$_2$ atmosphere at 425 °C in order to anneal the dielectric film and also to form the ohmic contact on back of the silicon wafer. After annealing, no significant difference in the results were observed between the samples prepared with e-gun or thermal evaporation of the gate electrodes. The resistivity of the film obtained was typically 10^{15} Ω-cm at an applied electric field of 5×10^5 V cm^{-1}. It has been claimed by Sibran et al.[12] that high bulk resistivity films can only be obtained with the

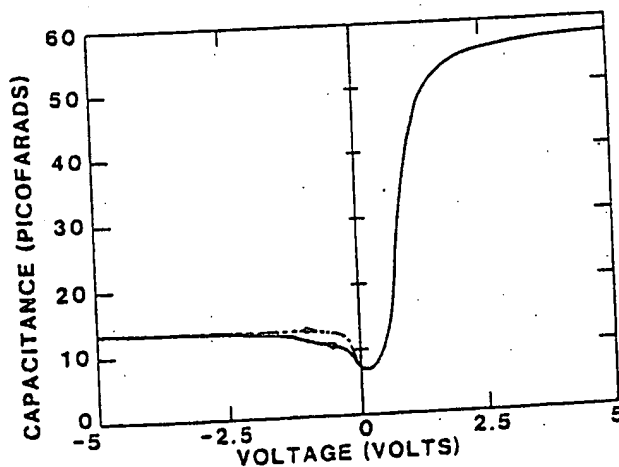FIG. 2. X-ray diffraction pattern of AlN film deposited on Si. Figure shows (002) peak of the AlN film and the peak of (100) Si.

FIG. 4. High frequency (100 KHz) C-V curve of Al/AlN/Si structure. Curves were obtained with both positive and negative ramp rates.

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aid of a high oxygen concentration, up to 50%. However, our annealed AlN films have consistently exhibited bulk resistivities in excess of 10^{15} Ω-cm in spite of a much lower oxygen content. Typical breakdown fields were 6×10^6 V cm^{-1}.

High frequency C-V measurements were carried out on MIS capacitors. Typical voltage ramp rates were 10–100 mV sec^{-1} and the high frequency modulation amplitude was kept below 50 mV to avoid broadening of the C-V curves. Figure 4 shows a C-V curve obtained at a frequency of 100 kHz. Measurements were taken for both positive as well as negtive ramp rates. No hystereisis in the flat-band voltage was observed as long as the bias voltage was below $\pm$ 5V. A minor deviation in the value of the capacitance at the onset of inversion was observed. This is due to the differences in the relaxation times associated with the generation and elimination of the charges in the inversion layer. The capacitance at large positive values of bias voltages was found to be independent of the test frequency between 100 Hz and 1 MHz. Hence, the dielectric constant of AlN exhibits no frequency dispersion in that range.

The shape of the C-V curve in Fig. 4 shows that the Fermi level at the AlN–Si interface is not pinned by extrinsic surface states. The saturation of the capacitance at both large positive and negative bias voltages is due to the formation of accumulation and inversion layers respectively. This
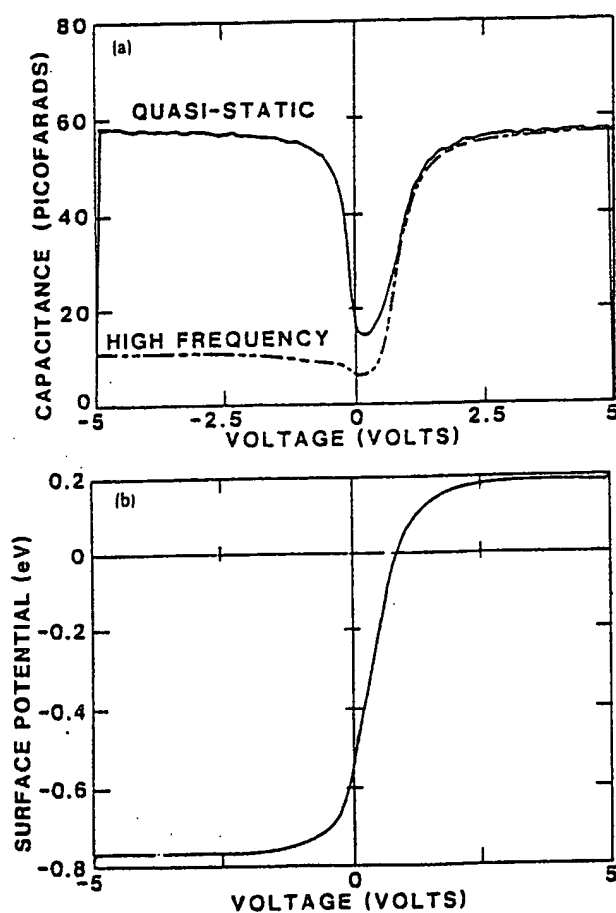
requires a swing in the surface potential across the entire band gap. Further evidence of this is presented by an analysis of the quasistatic C-V curves as described below.

An essentially zero frequency C-V curve can be obtained by a measurement of the displacement current at a constant ramp rate. This technique was used to investigate the Al/AlN/Si MIS structures and a typical result is illustrated in Fig. 5(a). Formation of the inversion layer is evidenced by the sharp turn on at 0.1 V, asymmetry in the dip, and identical values of capacitance in both accumulation and inversion. By using the integral method of Kuhn,[13] this curve was analyzed to determine the variation of the surface potential with bias voltage. This is shown in Fig. 5(b). A flatband voltage V_{fb} of 0.85 V was determined. This is close to those obtained by Morita et al.[14] and Hantzpergue et al.[15] These authors estimated theoretical V_{fb} to be 0.9 V for a Hg/AlN/Si system. The work function difference between Al and Hg is $-$ 0.25 V. Therefore, the expected V_{fb} for Al/AlN/Si is 0.65. Using this value of V_{fb} we calculated the density of fixed charge Q_{ss} in our sample to be 6×10^{10} cm^{-2}. This value of Q_{ss} is close to the minimum reported by Hantzpergue et al.,[15] and is well below the ones obtained by Gerova et al.[11] and Sibran et al.[12]

A comparison of the experimental quasistatic C-V curve with a theoretical one can be used to obtain a distribution of the surface states[13] across the entire band gap. Th result of such an analysis is illustrated in Fig. 6. A U-shaped distribution was obtained with a minimum at midgap. This minimum value of N_{ss} was determined to be 1.5×10^{11} cm^{-2} eV^{-1} and it compares favorably with the results of Morita et al.[14] who obtained the AlN film by the high temperature (1200 °C) process of metalorganic CVD. The distribution of surface states in the gap obtained in this investigation is in sharp contrast with the one obtained by Bouteville et al.[16] who observed a maximum in N_{ss} near midgap. However, these authors used CVD to obtain the AlN films.

The value of N_{ss} was found to depend on the oxygen content at the interface.[17] When the oxygen content at the interface was low (< 5%), generally we obtained higher values of N_{ss} (5×10^{11} cm^{-2} eV^{-1}) with the same flat-band voltage of 0.85 V. It appears that the presence of an aluminum-oxy-nitride layer at the interface reduces the density of states.
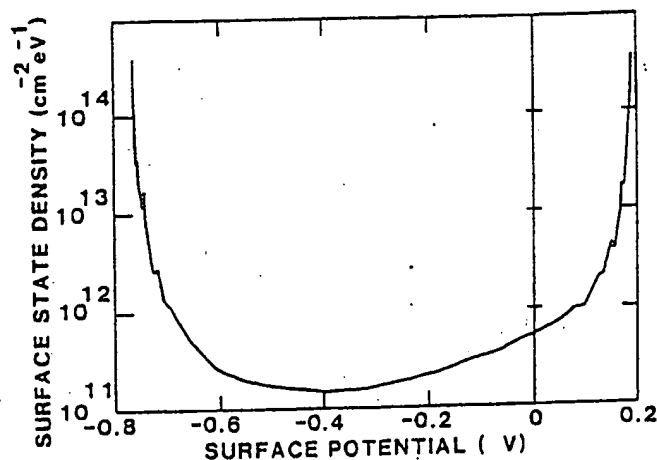

FIG. 5(a). Quasistatic C-V curve of Al/AlN/Si structure. (b) Variation of surface potential with applied bias. The surface potential is measured with respect to the Fermi level.

FIG. 6. Distribution of the surface states in the band gap.

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IV. CONCLUSION

Reactive rf magnetron sputtering in an $Ar:N_2$ gas mixture was used to deposit films of AlN. The films were found to be c axis orientated on crystalline and noncrystalline substrates. Sputter AES analysis was used to confirm the composition and the homogeneity of the film which generally contained less than 5% oxygen. The film exhibited bulk resistivities in excess of 10^{13} Ω cm. The AlN/Si interface was characterized by a fixed charge density of 6×10^{10} cm^{-2} and a flat-band voltage of 0.85 V. Detailed analysis for the density of fast interface states has been carried out. A U-shaped curve was obtained across the band gap with a minimum at midgap of 1.5×10^{11} cm^{-2} eV^{-1}. This study has demonstrated that AlN films can be obtained with reactive rf magnetron sputtering at substrate temperatures well below 400 °C. These films which exhibit high bulk resistivities, large breakdown fields and low density of surface states are suitable as gate dielectric for metal-insulator-semiconductor field-effect transistors (MISFETs).

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